(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 517 927 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent: **02.06.1999 Bulletin 1999/22**

(21) Application number: **92901918.0**

(22) Date of filing: **25.12.1991**

(51) Int Cl.[6]: **C08L 69/00**, C08L 83/10, C08L 101/00, C08L 27/12, C08L 25/04, C08L 23/00, C08L 77/00, C08L 67/00, C08L 21/00

(86) International application number: **PCT/JP91/01755**

(87) International publication number: **WO 92/12208 (23.07.1992 Gazette 1992/19)**

(54) **POLYCARBONATE RESIN COMPOSITION**

POLYCARBONATHARZZUSAMMENSETZUNG

COMPOSITION DE RESINE POLYCARBONATE

(84) Designated Contracting States: **BE CH DE FR GB IT LI NL SE**

(30) Priority:
27.12.1990 JP 415108/90
27.12.1990 JP 415109/90
27.12.1990 JP 415110/90
27.12.1990 JP 415111/90

(43) Date of publication of application: **16.12.1992 Bulletin 1992/51**

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Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a polycarbonate resin composition, and more particularly to a polycarbonate resin composition excellent in impact resistance, fluidity, solvent resistance, wear resistance and sliding characteristics, which comprises a novel polycarbonate-polydimethylsiloxane (PC-PDMS) copolymer and at least one of the group of thermoplastic crystalline resin, thermoplastic amorphous resin, fluorine resin and rubber-like elastomer.

Background Arts

[0002] Generally, polycarbonate resins are excellent in impact resistance, and improvement of them by blending with other resins have been widely attempted. For example, crystalline resins such as polyester and polyamide are added to improve the solvent resistance of a polycarbonate resin. However, mere addition of crystalline resin had a problem in lowering impact resistance, although solvent resistance is improved. To overcome the above problem. a composition obtained by blending polyalkylene terephthalate and polycarbonate-polysiloxane copolymer are blended with polycarbonate (Japanese Patent Application Laid-Open No. 215652/1986), a composition comprising polycarbonate-polysiloxane copolymer and polyamide (Japanese Patent Application Laid-Open No. 213557/1988) and so on have been proposed. Both the polycarbonate resin compositions, however, had a problem in that they were poor in heat resistance, although improved in impact resistance.

[0003] Further, attempts have been proposed to improve polycarbonate resins in low-temperature impact property by adding a thermoplastic amorphous resin such as acrylonitrile-butadiene-styrene (ABS), and styrene-maleic anhydride copolymer (SMA). By mere addition of thermoplastic amorphous resin, however, the impact resistance of the resulting polycarbonate resin was insufficient. In order to overcome above problem, a polycarbonate resin comprising polycarbonate-polysiloxane copolymer, acrylonitrile-butadiene-styrene (ABS) and acrylonitrile-styrene (Japanese Patent Application No. 287956/1986), and a polycarbonate resin comprising polycarbonate-polysiloxane copolymer, and styrene-maleic anhydride copolymer (SAM) (Japanese Patent Application Laid-Open No. 146952/1987) have been proposed. Both of these polycarbonate resin compositions, however, had a problem in that they are poor in Izod impact resistance.

[0004] Moreover, attempts to improve the sliding characteristics of polycarbonate resin by adding fluorine resin, for instance, have been made. Polycarbonate resin compositions resulted by these attempts are, for example, a polycarbonate resin comprising polycarbonate-polysiloxane copolymer, styrene-maleic anhydride copolymer (SMA), phosphide and polytetrafluoroethylene (Japanese Patent Application No. 277464/1987), and a polycarbonate comprising polycarbonate-polysiloxane copolymer, SMA and the like, phosphide, Teflon and acrylonitrile-butadiene-styrene (ABS) (Japanese Patent Application No.285948/1987). In these polycarbonate resin composition, however, though impact resistance was improved by the use of polycarbonate-polysiloxane, the effect of the improvement was not sufficient.

[0005] Furthermore, attempts have been made to improve impact resistance of polycarbonate resin by adding rubber-like elastomer. However, by mere addition of rubber-like elastomer, improvement in impact resistance could not be expected in a range where strength and elasticity of polycarbonate resin were not largely lowered. Polycarbonate resins which are improved iii the above problem are a polycarbonate resin comprising polycarbonate-polysiloxane and acrylic rubber or graft copolymer to polydimethyl siloxane (PDMS), and rubber (Japanese Patent Application No. 200161/1986) and a polycarbonate resin comprising polycarbonate-polysiloxane and isobutylene (Japanese Patent Application No. 51452/1988). In these polycarbonate resin compositions, however, impact resistance is improved since polycarbonate-polysiloxane was used, but the effect in the improvement was small.

[0006] In the state of art are further polycarbonate resins disclosed which do not fulfill the requirements of impact resistance.

[0007] In DE-A-39 08 038 compositions are disclosed having (A) 75 to 98.99 parts by weight of a polydiorganosiloxane-polycarbonate block copolymer, (B) 1 to 10 parts by weight of a graft copolymer of an ethylenic monomer on a rubber and/or (C) a rubber-like elastomer, and (D) 0.01 to 5 parts by weight of a low-molecular weight polysiloxane comprising phenyl residues. The polydiorganosiloxane structure units in the PDMS-PC-block copolymer have a molecular weight Mw of from 10.000 to 200.000 and a content of aromatic carbonate structure units between appr. 90 wt.% and 99.5 wt.% and a content of polydiorganosiloxane structure units between 10 wt.% and 0.5 wt.%.

[0008] EP-A-0261 382 discloses an incombustible impact-prove polycarbonate composition consisting of (A) 60 to 90 parts by weight of a halogen-free polydiorganosiloxane-polycarbonate block copolymer with a molecular weight Mw of from 10.000 to 200.000 and a content of aromatic carbonate structure units between 75 and 99 wt.% and a content of diorganosiloxane units between 25 and 1.0 wt.%, (B) 10 to 40 parts by weight of a halogen-free thermoplastic copolymer of from 50 to 95 wt.% styrene, α-methylstyrene, nucleus-substituted styrene or mixtures thereof and 5 to 50 wt.% (meth)acrylic nitrile, (C) 1 to 20 parts by weight, based on 100 parts by weight of the total weight of (A) and

(B), of a halogen-free phosphoric compound as defined therein, and (D) 0.5 to 5 wt.%, based on 100 parts by weight of the total weight of (A) and (B), of a tetrafluoro ethylene polymer having a density of from 2.0 to 2.3 g/cm^3 and a particle size of from 100 to 1.000 µm.

[0009] EP-A-0 260 559 discloses a composition comprising (A) 5 to 98 parts by weight of one or more thermoplastic polycarbonates, (B) 2 to 70 parts by weight of one or more graft polymers as defined therein, and (C) 0 to 80 parts by weight of thermoplastic copolymer as defined therein. US-PS-4,945,148 discloses silicone-polycarbonate block copolymers which are flame retardant and are useful as a dielectric film.

[0010] EP-A-0 188 791 discloses a composition of an aromatic polycarbonate resin comprising (a) an aromatic polycarbonate resin, (b) a polyalkylene terephthalate resin and/or an amorphous copolyester resin, and (c) a modifier which comprises a block copolymer comprising (i) blocks derived from an aromatic polycarbonate, and (ii) blocks derived from diorganopolysiloxane. Components (d) and (c) are present in such quantities that the composition has reduced melt viscosity and similar or better impact properties in the composition to the polycarbonate.

[0011] In US-PS-4,161,469 a polymer blend is disclosed comprising a polyalkylene terephthalate resin and an organosiloxane-polycarbonate block copolymer having an impact value greater than the impact value of the polyalkylene terephthalate resin component of the blend.

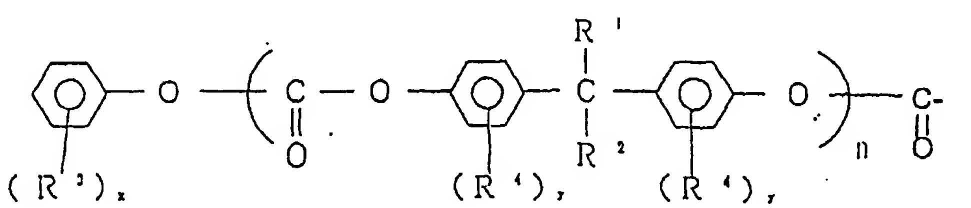
Disclosure of the Invention

[0012] Recently, the group of the present Inventors have succeeded in developing a novel polycarbonate copolymer having a new structure which is improved in impact strength while maintaining the mechanical and optical properties inherent in the conventional polycarbonate (the Specification of WO91/00885). The present inventors have repeated earnest investigations to improve the quality of said novel polycarbonate copolymer while maintaining the advantages of the novel polycarbonate copolymer.

[0013] As the result, it was found that the novel polycarbonate copolymer can be further improved in impact resistance by blending a thermoplastic resin including a thermoplastic crystalline resin, thermoplastic amorphous resin and a fluorine resin, or a rubber-like elastomer, while improving fluidity, solvent resistance, wear resistance, sliding characteristics and heat resistance. The present invention has been accomplished based on such a finding.

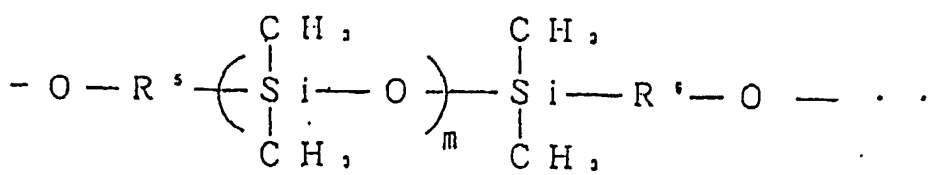
[0014] The present invention provides a polycarbonate resin composition which comprises

(A) 1 to 99 % by weight, 1 to 99 % by weight, 60 to 99 % by weight and 40 to 99 % by weight, respectively, of a polycarbonate/polydimethylsiloxane copolymer comprising a polycarbonate block represented by the general formula (a):



(a)

wherein R^1 and R^2 indicate independently a hydrogen, an alkyl group having 1 to 4 carbon atoms, R^3 and R^4 indicate independently a hydrogen, a halogen, or an alkyl group or an aryl group having 1 to 20 carbon atoms, x indicates an integer of 1 to 5, y indicates an integer of 1 to 4, and n indicates an integer of 1 to 100, and a polydimethylsiloxane block represented by the general formula (b):



(b)

wherein R^5 and R^6 indicate independently an organic residue containing aromatic nucleus, and m indicates an integer of 100 or larger,

said copolymer having 0.5 to 10 % by weight of polydimethylsiloxane block portion and 1.0 % by weight or less of

n-hexane soluble content, and a viscosity average molecular weight of 10,000 to 50,000 and
(B) at least one member selected from the group consisting of

99 to 1 % by weight of a thermoplastic crystalline resin,
99 to 1 % by weight of a thermoplastic amorphous resin,
40 to 1 % by weight of a fluor ne resin and
60 to 1 % by weight of a rubber-like elastomer.

[0015] Specifically. the present invention provides a polycarbonate resin composition comprising (A) 1 to 99% by weight of the above-mentioned polycarbonatepolydimethylsiloxane (PC-PDMS) copolymer and (B) 99 to 1% by weight of a thermoplastic crystalline resin.

[0016] The present invention also provides a polycarbonate resin composition comprising (A) 1 to 99% by weight of the above-mentioned polycarbonate-polydimethylsiloxane (PC-PDMS) copolymer and (C) 99 to 1% by weight of a thermoplastic amorphous resin.

[0017] Moreover, the present invention also provides a polycarbonate resin composition comprising (A) 60 to 99% by weight of the above-mentioned polycarbonate-polydimethylsiloxane (PC-PDMS) copolymer and (D) 40 to 1% by weight of a fluorine resin.

[0018] Further, the present invention also provides a polycarbonate resin composition comprising (A) 40 to 99% by weight of the above-mentioned polycarbonate-polydimethylsiloxane (PC-PDMS) copolymer and (E) 60 to 1% by weight of a rubber-like elastomer.

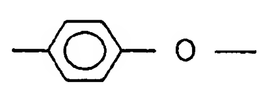
Best Mode for Carrying Out the Invention

[0019] The composition of the present invention comprises as the main ingredients (A) polycarbonate/polydimethylsiloxane (PC-PDMS) copolymer and (B) at least one selected from the group of thermoplastic resin and rubber-like elastomer. as described above.

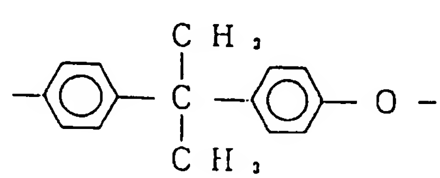
[0020] Herein PC-PDMS copolymer as component (A) is a block copolymer comprising a polycarbonate (hereinafter sometimes referred to as PC) block represented by the general formula (a) and a polydimethylsiloxane (hereinafter sometimes referred to as PDMS) represented by the general formula (b), as mentioned above.

[0021] R^1 and R^2 in the general formula (a) indicate independently a hydrogen, an alkyl group having 1 to 4 carbon atoms, such as a methyl group, an ethyl group, an n-propyl group. an i-propyl group, an n-butyl group. an i-butyl group, an s-butyl group, and a t-butyl group. R^3 and R^4 in the general formula (a) indicate independently a hydrogen, a halogen (such as chlorine. fluorine. or iodine). an alkyl having 1 to 20 carbon atoms (such as methyl group. ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, s-butyl group, t-butyl group, n-octyl group, t-octyl group, n-decyl group, and n-octadecyl group) or an aryl group (such as phenyl group, benzyl group, and α, α-dimethylbenzyl group).

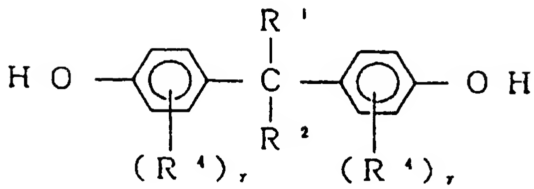
[0022] R^5 and R^6 in the general formula (b) are organic residues each containing an aromatic nucleus. Herein organic residues containing aromatic nucleus include various ones such as 3-(o-hydroxyphenyl)propylene group, 2-(p-hydroxyphenyl)ethylene group and groups represented by the formula:



and the formula:

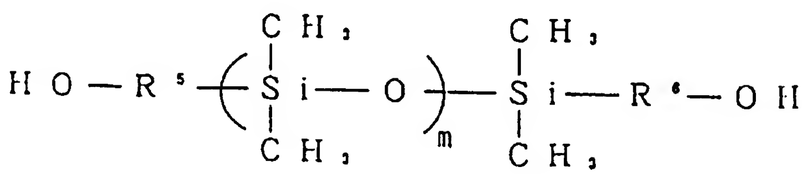


[0023] PC-PDMS copolymer as component (A) can be obtained by reaching, for example, an organic dihydroxy compound represented by the general formula (c):



· · (c)

(wherein R^1, R^2, R^4 and y are as defined above),a polydimethylsiloxane represented by the general formula (d):

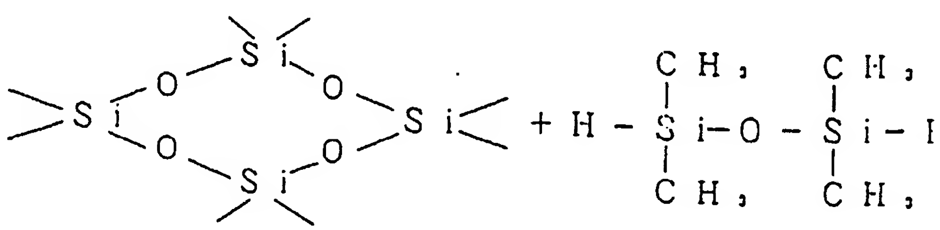


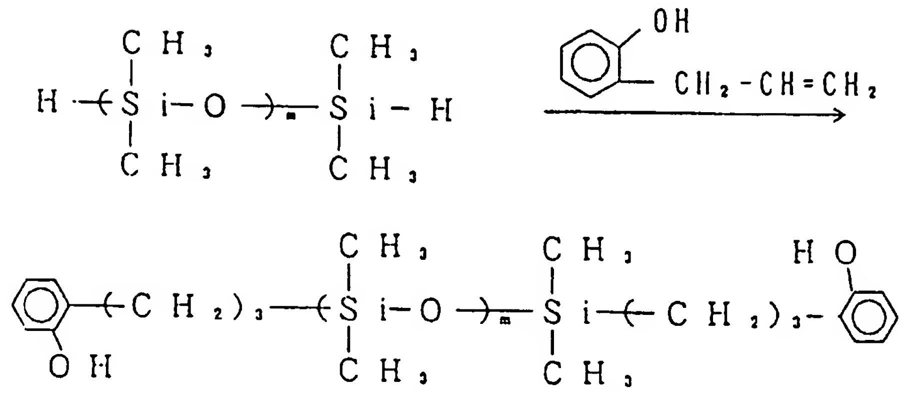
· · (d)

(wherein R^5, R^6 and m are as defined above),and a carbonic ester-forming derivative in a liquid medium in the presence of a molecular weight modifier.

[0024] Herein organic dihydroxy compounds represented by the general formula (c) include various ones such as bis(4-hydroxyphenyl)alkane. More specifically, they include bisphenols such as 2,2-bis(4-hydroxyphenyl)propane [commonly called bisphenol A], bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)pentane, 2,2-bis(4-hydroxyphenyl)isopentane, 2,2-bis(4-hydroxyphenyl) hexane, 2,2-bis(4-hydroxyphenyl)isohexane, 4,4-dihydroxytriphenylmethane, 4,4-dihydroxytetraphenylmethane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 2,2-bis(4,4-hydroxy-3-methylphenyl)propane, and 2,2-bis(4,4-hydroxy-3,5-dimethylphenyl)propane.

[0025] Polydimethylsiloxanes represented by the general formula (d) can be prepared as follows, Octamethylcyclotetrasiloxane and disiloxane, for instance, are reacted to form a polydimethylsiloxane having hydrogens at the terminals, which is reacted with arylphenyl. Thus polydimethylsiloxane having phenol groups at the terminals can be prepared. Therein the repeating number of dimethylsilanoxy units can be controlled by the ratio by volume of octamethylcyclotetrasiloxane and disiloxane. The above process for production is shown by the following reaction formulae.





[0026] The repeating number of dimethylsilanoxy unit m should be not less than 100. If m is less than 100, when, for example, the resulting product is blended with glass fiber as a filler, the Izod impact resistance of the resulting composition is insufficient. If m is in excess of 400, such a polydimethylsiloxane is difficult to prepare, and is not practical.

[0027] After the completion of the reaction, vacuum distillation is desirably conducted to remove the low boiling point components (mainly dimer or trimer). Conditions for the vacuum distillation are not limited particularly, but distillation is conducted at 100 to 200°C under 10 or less Torr (about 1 to 200 minutes) until low boiling point component is not distilled out.

[0028] As the carbonic ester-forming derivative, phosgene is usually used, but in addition to said phosgene, various compounds such as bromophosgene, diphenyl carbonate, di-p-tolyl carbonate, phenyl-p-tolyl carbonate, di-p-chlorophenyl carbonate, and dinaphtyl carbonate, and moreover, a polycarbonate oligomer comprising such a compound and an organic dihydroxy compound mentioned before can also be used.

[0029] In the present invention, when PC-PDMS copolymer is produced from an organic dihydroxy compound, polydimethylsiloxane, and carbonic ester-forming derivative as mentioned above, a molecular weight modifier should be exist in the reaction system. Therein various molecular weight modifiers can be used. Specific examples of the molecular weight modifiers are pentahalogenophenol (such as pentabromophenol, pentachlorophenol, pentafluorophenol), trihalogenophenol (such as tribromophenol, trichlorophenol, and trifluorophenol), phenol, p-cresol, p-tert-butylphenol, p-tert-octylphenol, and p-cumylphenol.

[0030] The amount of the organic dihydroxy compound to be placed in may be selected properly depending on the polymerization degree of polycarbonate block to be produced. On the other hand, since the amounts of the molecular weight modifier and the carbonic ester-forming derivative to be introduced define the polymerization degree of polycarbonate block, these amounts should be selected according to the purpose. The specific amount of molecular weight modifier to be introduced may be selected around an amount enough to be combined with the terminal (particularly both the terminals) of the resulting polycarbonate or an amount somewhat larger than the same.

[0031] Polydimethylsiloxane is preferably contained so as to exist in a proportion of 0.5 to 10% by weight, particularly 1 to 10% by weight in the copolymer. If the proportion is less than 0.5% by weight, the Izod impact resistance of the resulting polycarbonate is insufficient when it is blended with glass fiber used as the filler, for instance. However, if the proportion is in excess of 10% by weight, the heat distortion temperature of the resulting polycarbonate will be low.

[0032] The PC-PDMS copolymer to be used in the present invention can be produced by conducting the reaction in an aqueous medium. Specifically, the reaction may proceed in accordance with the interface polymerization method, the pyridine method and the like which are conventionally known.

[0033] The copolymer comprising PC block represented by the general formula (a) and PDMS block represented by the general formula (b) which are obtained as above has a viscosity average molecular weight of 10,000 to 50,000, preferably 12,000 to 30,000. If viscosity average molecular weight is less than 10,000, the Izod impact strength of the copolymer is too low to comply with the object of the present invention. However, copolymers of which viscosity average molecular weight is in excess of 50,000 have difficulty in their production process.

[0034] In the PC-PDMS copolymer of the present invention, n-hexane soluble content is 1.0% by weight or smaller. Therein if n-hexane soluble content is in excess of 1.0% by weight, when the copolymer is blended with inorganic filler such as glass fiber, Izod impact resistance is not so improved. Particularly, in order to increase the effect of improvement in Izod impact resistance when the copolymer is blended with glass fiber and the like, PC-PDMS copolymer having a crystallization degree of 30% or higher is preferable.

[0035] In order to produce said PC-PDMS copolymer having a n-hexane soluble content of 1.0% by weight or smaller, for example, the copolymerization reaction as mentioned above should be conducted while controlling the PDMS con-

tent in the copolymer to 10% by weight or smaller, and with the use of PDMS having 100 or more of the dimethylsilanoxy repeating unit, and with the use of 5.3 x 10-3 mol/kg. oligomer or more of a catalyst such as tertiary amine.

[0036] Component (B) to be used in the present invention comprises at least one selected from the group of thermoplastic resin and rubber-like elastomer. The thermoplastic resin includes thermoplastic crystalline resin, thermoplastic amorphous resin and fluorine resin.

[0037] The thermoplastic crystalline resin, one of Component (B) to be used in the present invention includes polyester resin, polyamide resin, and polyolefin resin.

[0038] As the polyester resin therein, various ones can be used, but polyester resin obtained by polycondensation of bifunctional carboxylic acid component and alkylene glycol component is preferably used. Suitable examples of these polyester resins are polyethylene terephthalate (PET), and polybutylene terephthalate (PBT).

[0039] Said polyester resins can be produced by a usual method in the presence or absence of a polycondensation catalyst which contains titanium, germanium, antimony or the like. For example, polyethylene terephthalate is produced by a so-called two-step polymerization reaction. Said two-step polymerization reaction comprises the first step reaction in which terephthalic acid and ethylene glycol are esterified, or a lower alkyl ester of terephthalic acid such as dimethylterephthalate and ethylene glycol are esterified to produce the glycol ester of terephthalic acid and/or the low polymer thereof; and the second step reaction in which said glycol ester and/or its low polymer are further polymerized to produce a polymer of higher polymerization degree.

[0040] The bifunctional carboxylic acid component and alkylene glycol component to be used in the above reaction are as follows. Example of bifunctional carboxylic acid component is aromatic carboxylic acid such as terephthalic acid, isophthalic acid, and naphthalene dicarboxylic acid. Among these, terephthalic acid is preferable, and other bifunctional carboxylic acid component can be used in combination so far as the effect of the present invention is not impaired. Further examples of bifunctional carboxylic acid are aliphatic dicarboxylic acid such as oxalic acid, malonic acid, adipic acid, suberic acid, azelaic acid, sebacic acid and decanedicarboxylic acid, and ester forming derivatives thereof. Preferable proportion of these dicarboxylic acid components other than terephthalic acid is usually within 20 mol% of the total dicarboxylic acid.

[0041] As the above-mentioned alkylene glycol component, for example, aliphatic diols containing 2 to 15 carbon atoms, such as ethylene glycol, propylene-1,2-glycol, propylene 1,3-glycol, butylene-1,4-glycol, butylene-2,3-glycol, hexane 1,6 diol, octane-1,8-diol, neopentyl glycol and decane-1,10-diol can be used. Among these, ethylene glycol, and butylene glycol are suitable.

[0042] Various polyamide resins can be used there. For example, all of open-ring polymer of lactam. polycondensate of diamine and dibasic acid, and polycondensate of ω-amino acid can be used, and also mixtures of these polymers, and copolymer thereof can be used. Specific example of them are Nylon-6 (PA6), Nylon-4.6, Nylon-6.6, Nylon-6.10, Nylon-6.12, Nylon-11, Nylon-12, and Nylon-6/6.6 copolymer.

[0043] Further, examples of polyolefin resins to be used therein are homopolymers of olefin such as α-olefin, including ethylene, propylene, butene-1, isobutylene, pentene-1, 3-methylbutene-1,4-methylpentene-1, hexene-1, and octene; copolymers of two or more these olefins; and copolymers of olefin with vinyl compound, unsaturated carboxylic acid, unsaturated carboxylic acid ester or the like comprising 70 mol% or more, preferably 80 mol% or more of olefin, for example, copolymers of olefin with vinyl compound including vinyl esters such as vinyl acetate or vinyl halide such as vinyl chloride, copolymers of olefin with unsaturated carboxylic acid such as acrylic acid, methacrylic acid, and maleic acid, or copolymers of olefin with unsaturated carboxylic acid ester such as methyl acrylate, ethyl acrylate. methyl methacrylate, and ethyl methacrylate. Specific examples of them are low density polyethylene, linear low density polyethylene, high density polyethylene (HDPE), isotactic polypropylene, atactic polypropylene, an ethylene-propylene copolymer, an ethylene-vinyl acetate copolymer, or saponified product thereof, an ethylene-methyl acrylate copolymer, ethylene-ethylacrylate copolymer, and ethylene-methyl methacrylate copolymer.

[0044] In the composition of the present invention, the proportions of Component (A) and Component (B), when thermoplastic crystalline resin is used as Component (B), are usually 1 to 99% by weight and 99 to 1% by weight, respectively. More preferably, 30 to 95% by weight of Component (A) and 70 to 5% by weight of Component (B) are blended. If Component (A) is less than 1% by weight, the original impact resistance of PC-PDMS copolymer does not reveal sufficiently, while if it is in excess of 99% by weight, no improvement in fluidity and solvent resistance are obtained.

[0045] As thermoplastic crystalline resin, one of Component (B), various ones including styrene-based resin can be used. Examples of the styrene-based resins are general purpose polystyrene resin (GPPS), high impact resistant polystyrene resin (HIPS), styrene-maleic acid anhydride copolymer (SMA), and acrylonitrile-butadiene-styrene resin (ABS).

[0046] Specific examples of the above-mentioned high resistant polystyrene resin are a polymer containing a soft component in dispersed form, obtained by dissolving or mixing a rubber-like elastomer in or with monovinyl aromatic monomer, and then polymerizing them. As the rubber-like elastomer, polybutadiene is particularly preferred. In addition, styrene-butadiene-styrene (SBS) resin, acrylonitrile-styrene-butadiene (ASB) resin, styrene-butadiene copolymer rubber (SBR), butadiene-acryl rubber, isoprene rubber, isoprene-styrene rubber, isoprene-acryl rubber, and ethylene-pro-

pylene rubber are also preferred. The polybutadiene to be used herein may be any of low cis-polybutadiene (for example, those containing 1 to 30 mol% of 1,2-vinyl bond, and 30 to 42 mol% of 1,4-cis bond), high cis polybutadiene (for example, those containing less than 20 mol% of 1,2-vinyl bond, and 78 mol% or more of 1,4-cis bond), or may be mixture thereof.

[0047] In the above-mentioned styrene/maleic anhydride copolymer, the ratio of the two components can vary in a wide range, and so is molecular weight. Styrene-maleic anhydride copolymer can generally be produced by reacting maleic anhydride and styrene in the presence of peroxide catalyst while temperature is elevated (see the specifications of US Patent Nos. 2,866,771 and 2,971,939). Said copolymer may contain, in place of styrene itself, α-methylstyrene, vinyltoluene, 2,4-dimethylstyrene, chlorostyrene or other substituted styrenes. The molecular weight of the styrene-maleic anhydride copolymer can be selected from a wide range. It can vary, for example, in the range of 20,000 to 300,000, preferably approximately 80,000 to 200,000. The styrene/maleic anhydride copolymer preferably contains for instance 5 to 50% by weight, more preferably 5 to 30% by weight, still more preferably 8 to 15% by weight of maleic anhydride. Therein rubber-modified styrene/maleic anhydride copolymer can be used. Said rubber-modified styrene/maleic anhydride copolymer is obtained by thermal polymerization of styrene monomer and maleic anhydride using a rubber component in the presence of a chain-transfer agent, and a radical generator.

[0048] Typical examples of the rubber components are, for example, butadiene rubber, butadiene-styrene rubber or butadiene-acrylic rubber containing 60 to 95% by weight of butadiene, isoprene rubber, isoprene-styrene rubber or isoprene-acrylic rubber containing 60 to 95% by weight of isoprene, A-B type block rubber or A-B-A type block rubber of butadiene-styrene containing 50 to 95% by weight of butadiene, and ethylene-propylene copolymer rubber (EPT). These are used as mixture of one or two kinds.

[0049] The rubber component as above is preferably contained in a proportion of 2 to 25% by weight, preferably 5 to 12% by weight in the rubber-modified copolymer obtained finally.

[0050] In the above ABS resin, as the rubber-like polymer to be used for producing graft copolymer, polybutadiene or butadiene copolymer is used alone or as a mixture. Herein, as butadiene copolymer, copolymers of butadiene and vinyl monomer (such as styrene, and acrylonitrile). Said vinyl monomers to be graft-polymerized on rubber-like polymer are mixtures of two or more monomers selected from the group of aromatic vinyl monomer, vinyl cyanide monomer and methacrylic ester monomer. Aromatic vinyl monomers therein include, for example, styrene, vinyltoluene, vinylxylene, halogenated styrene; vinyl cyanide monomers include acrylonitrile, and methacrylonitrile; and methacrylate monomers include methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate.

[0051] These monomers often are used as mixtures of two kinds or more. Preferable combinations of them are, for example, styrene and acrylonitrile. styrene and methyl methacrylate, styrene and mixture of acrylonitrile and methyl methacrylate.

[0052] In the composition of the present invention shown as above, when thermoplastic amorphous resin is used as Component (B), usually 1 to 99% by weight of Component (A) and 99 to 1% by weight of Component (B) are blended. Preferable proportions of Component (A) and Component (B) are 30 to 95% by weight, and 70 to 5% by weight, respectively. If the proportion of Component (A) is less than 1% by weight, the impact resistance originally belongs to PC-PDMS copolymer does not reveal sufficiently, and if it is in excess of 99% by weight, fluidity of the resulting composition is poor. If the proportion of Component (B) is less than 1% by weight, the resulting composition is not improved in fluidity, and if it is in excess of 99% by weight impact strength of the composition are poor.

[0053] As the fluorine resin to be used as Component (B) of the present invention, any resin that contains fluorine atom in the molecule thereof can be used. Particularly, resins having C-F bond in the molecule thereof, such as polytetrafluoroethylene, polychlorofluoroethylene, polychlorotrifluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, a hexafluoropropylene-tetrafluoroethylene copolymer, and a chlorotrifluoroethylene/vinylidene fluoride copolymer are preferred, and among them polytetrafluoroethylene having a melting point of 300 to 350°C is particularly preferred.

[0054] In the composition of the present invention shown above, when fluorine resin is used as Component (B), 60 to 99% by weight of Component (A) and 40 to 1% by weight of Component (B) are usually blended. Preferably, 65 to 95% by weight of Component (A) and 35 to 5% by weight of Component (B) are blended. If the proportion of Component (A) is less than 60% by weight, the original impact resistance of PC-PDMS copolymer does not reveal sufficiently, and if it is in excess of 99% by weight, the resulting composition is not so improved in wear resistance or sliding characteristics. If the proportion of Component (B) is less than 1% by weight, the resulting composition is not improved in wear resistance or sliding characteristics, and if it is in excess of 40% by weight, the appearance of the molding product is poor.

[0055] Further, rubber-like elastomers to be used as one of Component (B)s of the present invention include natural rubber, synthetic rubber, and graft copolymer.

[0056] Rubber-like elastomer used there is not particularly limited. For example, natural rubber (NR); diene-based rubber such as styrene-butadiene rubber (SBR), butyl rubber (BR), isoprene rubber (IR), nitrile-butadiene rubber (NBR), nitrile-isoprene rubber (NIR), and chloroprene rubber (CR); olefin-based rubber such as isobutylene-isoprene rubber (IIR), ethylene-propylene rubber (EPM), ethylene-propylene-diene rubber (EPDM), chlorosulfonated polyethylene rub-

ber (CSM), halogenated butyl rubber, styrene-butadiene block copolymer rubber, styreneisoprene block copolymer rubber, rubber-like chlorosulfonated polyethylene (CSM), rubber-like chlorinated polyethylene (CPE). acrylic rubber, copolymer of alkyl acrylate and 2-chloroethyl vinyl ether (ACM), copolymer of alkyl acrylate and acrylonitrile (ANM), urethane rubber (thermoplastic type), silicone rubber, fluorine rubber, polyester-polyether-polyester block copolymer rubber, epichlorohydrin rubber, and ethylene-vinyl acetate rubber (EVM); various acrylic rubber; and organic silicone compounds, organic fluorine compound-based rubber, urethane-based rubbers, and ether-based rubbers can be used. Further, MAS resin (graft copolymer of 60 to 80% by weight of n-butyl acrylate, and styrene and methyl methacrylate), MABS resin (copolymer obtained by copolymerizing octyl acrylate and b.utadiene in a weight ratio of 7:3 to form a rubber latex, and graft polymerizing styrene and methyl methacrylate onto the rubber latex), MBS resin (copolymer obtained by copolymerization of methyl methacrylate and butadiene to form a rubber latex, and then graft polymerizing styrene onto the rubber latex) and the like are mentioned.

[0057] In the composition of the present invention shown above, when a rubber-like elastomer is used as Component (B), usually 40 to 99% by weight of Component (A) and 60 to 1% by weight of Component (B) are blended. Preferably, 50 to 95% by weight of Component (A) and 50 to 5% by weight of Component (B) are blended. If the proportion of Component (A) is less than 40% by weight, impact resistance inherent to PC-PDMS copolymer does not reveal sufficiently, and if it is in excess of 99% by weight, fluidity of the resulting composition is lowered. If the proportion of Component (B) is less than 1% by weight, the resulting composition is not improved in fluidity, and if it is in excess of 60 by weight, strength and elasticity of the composition are lowered.

[0058] In the polycarbonate resin composition of the present invention, various inorganic fillers, additives or other synthetic resins, elastomers and the like can be blended if necessary, so far as the object of the present invention is not impaired.

[0059] Examples of above-mentioned inorganic fillers to be blended to increase the mechanical strength, durability or volume of the polycarbonate resin composition are glass fiber (GF), glass beads, glass flake, carbon black, calcium sulfate, calcium carbonate, calcium silicate, titanium oxide, alumina, silica, asbestos, talc, clay, mica, and quartz powder. Examples of the additives are antioxidants including hindered phenol-based ones, phosphorous (such as phosphorous ester and phosphoric ester)-based ones, ultraviolet ray absorbers including benzotriazole-based, and benzophenone-based ones; external lubricants such as aliphatic carboxylate, and paraffin based ones; usual flame retardands; releasing agents; antistatic agents; coloring agents and the like. As the above hindered phenol-based antioxidant, BHT (2,6-di-tertiary-butyl-p-cresol), IRGANOX 1076 and IRGANOX 1010 (trade names, both produced by Ciba Geigy Corporation), ETHYL 330 (trade name, produced by Ethyl Corporation), and Sumilizer GM (trade name, produced by Sumitomo Chemical Co., Ltd.) are preferably used.

[0060] The polycarbonate resin composition of the present invention can be obtained by blending and kneading the above-mentioned components. Blending and kneading can be conducted by the conventional methods by the use of a ribbon blender, a Henschel mixer, a Banbury mixer, a drum tumbler, a single screw extruder, a twin screw extruder, a cokneader, and multi-screw extruder, for instance. Preferable temperature at kneading is usually 250 to 300°C.

[0061] The polycarbonate resin composition thus obtained can be molded by various conventional molding methods such as injection molding, extrusion molding, compression molding, calender molding. and rotary molding to produce moldings for cars such as bumpers. and moldings for home electric appliances.

[0062] The polycarbonate resin composition of the present invention is excellent in solvent resistance and fluidity (flow value is large) as well as impact resistance, and suitable for interior material and exterior material particularly for cars. In the field of office automation apparatus, it is suitable for chassis and housing material. Further, particularly it is suited for sliding part of gears and toothed wheels.

[0063] The present invention will be described in greater detail with reference to the following examples.

<u>Preparation Example 1</u>

(Preparation of PDMS with phenol groups at terminals)

[0064] 1483 g of octamethylcyclotetrasiloxane and 18.1 g of 1,1,3,3-tetramethyldisiloxane, and 35 g of 86% sulfuric acid were mixed, and stirred for 17 hours at room temperature. Subsequently, the oil phase was separated, and 25 g of sodium hydrogencarbonate was added, and the mixture was stirred for 1 hour. After filtration, the mixture was vacuum distilled at 150 °C under 3 torr, and low boiling point matters were removed.

[0065] To the mixture of 60 g of 2-allylphenol and 0.0014 g of platinum chloride-alcoholate complex, 294 g of the oil obtained as above was added at a temperature of 90°C. The resulting mixture was stirred for 3 hours while kept in the temperature range of 90 to 115 °C . The resulting product was extracted with methylene chloride, washed three times with 80% aqueous methanol to remove excessive 2-allylphenol. The residue was dried with anhydrous sodium sulfate, and the solvent was distilled away under vacuum up to a temperature of 115 °C.

[0066] Determination by nuclear magnetic resonance (NMR) showed that the repeating number of dimethylsilanoxy

unit of the PDMS with phenol groups at terminals obtained was 150.

Preparation Example 2

(Preparation of Polycarbonate Oligomer of Bisphenol A)

[0067] Into 400 ℓ of 5% aqueous solution of sodium hydroxide, 60 kg of bisphenol A was dissolved to prepare an aqueous solution of sodium hydroxide of bisphenol A. Subsequently, said aqueous solution of sodium hydroxide kept at room temperature was introduced at a flow rate of 138 ℓ /hour, and methylene chloride was introduced at a flow rate of 69 ℓ /hour into a tubular reactor having an inner diameter of 10 mm and a tube length of 10 m by way of an orifice plate, and phosgene was blown into the above as a parallel stream at a flow rate of 10.7 kg/hour, and continuously reacted for 3 hours.

[0068] The tubular reactor used here had double tubes, and cooling water was flowed in the jacket part to keep the reaction solution at an exhaustion temperature of 25 °C. The exhausted solution was adjusted to show pH 10 to 11. After the reaction solution thus obtained was allowed to stand still, the aqueous phase was separated and removed, and methylene chloride phase (220ℓ) was taken up. To the methylene chloride, further 170ℓ of methylene chloride was added and fully stirred. The resulting mixture was polycarbonate oligomer (concentration : 317 g/ℓ). The polymerization degree of the polycarbonate oligomer obtained therein was 3 to 4.

Preparation Examples 3 to 5

[0069] 91 g of reactive PDMS obtained by Preparation Example 1 was dissolved into 2ℓ of methylene chloride to be mixed with 10ℓ of PC oligomer obtained in Preparation Example 2. Thereto, a solution obtained by dissolving 26 g of sodium hydroxide in 1ℓ of water, and b (cc) of triethyl amine (TEA) were added and stirred at 500 rpm for 1 hour at room temperature. Then, a solution obtained by dissolving 600 g of bisphenol A into 5ℓ of 5.2% by weight aqueous solution of sodium hydroxide, and 8ℓ of methylene chloride and a (g) of p-tert-butylphenol (PTBP) were added further, and the resulting mixture was stirred at 500 rpm at room temperature for 2 hours. After that, 5ℓ of methylene chloride was added further, and the mixture was washed with 5ℓ of water, alkali washed with 5ℓ of 0.01 N aqueous solution of sodium hydroxide, acid washed with 5ℓ of 0.1 N chloric acid, and washed with 5ℓ of water in turn, and lastly methylene chloride was removed to obtain PC-PDMS copolymer in chipped form. The PC-PDMS copolymer obtained was tested for its properties under the following conditions.

Determination of PDMS content and PDMS chain length (dimethylsilanoxy unit)

[0070] PDMS content was found by the intention ratio of the peak ascribable to methyl group in the isopropyl of bisphenol A observed at 1.7 ppm, and the peak ascribable to methyl group in dimethylsiloxane observed at 0.2 ppm of ^{1}HNMR.

[0071] The chain length of PDMS was found by the intention ratio of the peak ascribable to methyl group in dimethylsiloxane observed at 0.2 ppm and the peak ascribable to the methylene group of PC-PDMS bond observed at 2.6 ppm by ^{1}HNMR.

Determination of n-hexane soluble content

[0072] It is a component extracted by Soxhlet extraction method with n-hexane as the solvent. Specifically, 15 g of chipped copolymer as sample was taken on cylindrical filter paper No. 84 (28 x 100 mm), and extracted by reflux for 8 hours in a reflux amount of once per 3 to 4 minutes (20 ml/time) by the use of 300 ml of n-hexane. After that, 300 ml of n-hexane was evaporated, and the residue was weighed and regarded as n-hexane soluble content.

[0073] The result is shown in Table 1.

Examples 1 to 11 and Comparative Examples 1 to 10

[0074] Prescribed amounts of PC-PDMS copolymer and thermoplastic crystalline resin shown in Tables 2 and 3 were premixed by a drum tumbler. then supplied to an extruder. kneaded at a temperature of 280 °C to obtain a polycarbonate resin composition. The composition was then pelletized.

[0075] Further, resulting pellet was injection-molded at a cylinder temperature of 280°C. and at a mold temperature of 80 °C to obtain a test piece.

[0076] The test piece was determined for Izod impact strength. tensile strength. solvent resistance, and the flow value of pellet. The results are shown in Tables 2 and 3.

[0077] Notes in Table 2 are as follows.

*1 PC-PDMS copolymer of Preparation Example 3
*2 PC-PDMS copolymer of Preparation Example 4
*3 Dianite MA-523, produced by Mitsubishi Rayon Co., Ltd.
*4 Toughpet N1000, produced by Mitsubishi Rayon Co., Ltd.
*5 Ube Nylon 1013. produced by Ube Industries, Ltd.
*6 Ube Nylon 2020, produced by Ube Industries, Ltd.
*7 Idemitsu Polyethylene 640UF, produced by Idemitsu Petrochemical Co., Ltd.
*8 Idemitsu Polypro J-465H, produced by Idemitsu Petroleum Co., Ltd.
*9 03MA409C (length : 3mm, diameter : 13μm), produced by Asahi Fiber Glass Co., Ltd.
*10 Flow Value at 280°C. Load : 160 kg
*a Percentage based on the total amount of PC-PDMS copolymer and thermoplastic crystalline resin
*b Proportion to the total amount of PC-PDMS copolymer and thermoplastic crystalline resin as 100 part by weight

Table 1

No.	PTBP a(g)	TEA b(cc)	Viscosity average molecular weight ($\times 10^4$)	Chain length of PDMS (m)	PDMS content (wt%)	n-hexane soluble content (wt%)
Preparation Example 3	119	5.7	1.5	150	2	0.4
Preparation Example 4	81	5.7	2.0	150	2	0.3
Preparation Example 5	119	1.2	1.5	150	2	1.4

Table 2

No.	PC-PDMS copolymer Kind	PC-PDMS copolymer Amount *a (wt%)	Thermoplastic crystalline Resin Kind	Thermoplastic crystalline Resin Amount *a (wt%)	Other Additives Kind	Other Additives Amount *b (part by weight)
Example 1	I *1	90	PET *3	10	–	–
Example 2	I	70	PET	30	–	–
Example 3	I	50	PET	50	–	–
Example 4	II *2	70	PET	30	–	–
Example 5	I	80	PBT *4	20	–	–
Example 6	I	60	PBT	40	–	–
Example 7	II	70	PBT	30	–	–
Example 8	I	70	PET	30	GF *9	10
Example 9	I	90	PA6 *5	10	–	–
Example 10	I	90	PA66 *6	10	–	–
Example 11	I	90	HDPE *7	10	–	–
Example 12	II	90	HDPE	10	–	–
Example 13	I	80	PP *8	20	–	–

Table 2 (continued)

No.	Result of Evaluation				
	Izod Impact Strength (kg·cm/cm)		Tensile Strength (kg/cm^2)	Solvent Resistance (Critical Strain) (%)	Flow Value*10 (ml/sec)
	(23°C)	(-30°C)			
Example 1	75	30	630	0.3	$50x10^{-2}$
Example 2	65	25	610	0.5	$60x10^{-2}$
Example 3	15	14	600	0.6	$70x10^{-2}$
Example 4	85	30	640	0.6	$10x10^{-2}$
Example 5	65	25	650	0.4	$70x10^{-2}$
Example 6	20	15	650	0.6	$85x10^{-2}$
Example 7	30	20	670	0.6	$14x10^{-2}$
Example 8	18	12	1100	0.45	$50x10^{-2}$
Example 9	6	4	680	0.35	–
Example 10	6	4	650	0.35	–
Example 11	55	30	550	0.70	$70x10^{-2}$
Example 12	65	35	570	0.80	$8x10^{-2}$
Example 13	40	15	250	2.5	$140x10^{-2}$

Table 3

No.	PC or PC-PDMS copolymer Kind	PC or PC-PDMS copolymer Amount (wt%)	Thermoplastic Crystalline Resin Kind	Thermoplastic Crystalline Resin Amount (wt%)	Other Additives Kind	Other Additives Amount (Part by weight)
Comparative Example 1	III *11	90	PET	10	–	–
Comparative Example 2	III	70	PET	30	–	–
Comparative Example 3	III	50	PET	50	–	–
Comparative Example 4	III	80	PBT	20	–	–
Comparative Example 5	III	60	PBT	40	–	–
Comparative Example 6	III	70	PET	30	GF	10
Comparative Example 7	III	90	PA6	10	–	–
Comparative Example 8	III	90	HDPE	10	–	–
Comparative Example 9	IV *12	70	PET	30	–	–
Comparative Example 10	IV	80	PBT	20	–	–

*11 Toughlon A2200 (molecular weight: 22,000) Polycarbonate (PC) produced by Idemitsu Petrochemical Co., Ltd.

*12 PC-PDMS copolymer of Preparation Example 5. (n-hexane soluble content: 1.4% by weight)

Table 3 (continued)

No.	Result of Evaluation				
	Izod Impact Strength (kg·cm/cm)		Tensile Strength (kg/cm^2)	Solvent Resistance (Critical Strain) (%)	Flow Value *13 (ml/sec)
	(23°C)	(-30°C)			
Comparative Example 1	85	20	630	0.3	8×10^{-2}
Comparative Example 2	75	15	600	0.5	10×10^{-2}
Comparative Example 3	15	10	590	0.6	12×10^{-2}
Comparative Example 4	75	15	640	0.4	12×10^{-2}
Comparative Example 5	15	10	650	0.6	16×10^{-2}
Comparative Example 6	10	8	1070	0.45	8×10^{-2}
Comparative Example 7	4	2	660	0.35	-
Comparative Example 8	55	20	550	0.70	8×10^{-2}
Comparative Example 9	75	18	610	0.5	60×10^{-2}
Comparative Example 10	75	18	650	0.4	70×10^{-2}

*13 Flow Value at 280°C, Load: 160 kg

Examples 12 to 21 and Comparative Examples 11 to 19

[0078] Prescribed amount of PC-PDMS copolymer and thermoplastic amorphous resin shown in Tables 4 and 5 were premixed by a drum tumbler, then supplied to an extruder and kneaded at 260°C to obtain a polycarbonate resin composition, which was pelletized.

[0079] The pellet obtained was injection molded at a cylinder temperature of 260°C and at a mold temperature of

80°C to obtain a test piece.

[0080] The test piece was determined for Izod impact strength, tensile strength. solvent resistance and flow value of the pellet. The results are shown in Tables 4 and 5.

[0081] Notes in Table 4 are as follows.

- *1 PC-PDMS in Preparation Example 3
- *2 PC-PDMS in Preparation Example 4
- *3 ABS resin comprising 28 parts by weight of butadiene, 24 parts by weight of acrylonitrile, and 48 parts by weight of styrene
- *4 Impact-resistant styrene/maleic anhydride copolymer (DYLARK D250, produced by Atlantic Richfield Co., Ltd., USA)
- *5 General purpose styrene/maleic anhydride copolymer (MOREMAX UG430, produced by Idemitsu Petrochemical Co., Ltd.)
- *6 General purpose polystyrene (Idemitsu Styrol HH30, produced by Idemitsu Petrochemical Co., Ltd.)
- *7 Impact resistant polystyrene (Idemitsu Styrol HT52, produced by Idemitsu Petrochemical Co., Ltd.)
- *8 03MA409C (length : 3 mm, diameter : 13 μ), produced by Asahi Fiber Glass Co., Ltd.
- *9 Flow value : 260 °C, Load : 100 kg
- *a Percentage based on the total amount of PC-PDMS copolymer and thermoplastic amorphous resin
- *b Proportion to the total amount of PC-PDMS copolymer and thermoplastic amorphous resin as 100 parts by weight

Table 4

No.	PC-PDMS copolymer		Thermoplastic Amorphous Resin		Other Additives	
	Kind	Amount*a (wt%)	Kind	Amount*a (wt%)	Kind	Amount*b (Part by weight)
Example 12	I*1	50	ABS*3	50	—	—
Example 13	I	70	ABS	30	—	—
Example 14	II*2	50	ABS	50	—	—
Example 15	I	60	HISMA*4	40	—	—
Example 16	I	40	HISMA	60	—	—
Example 17	II	80	GPSMA*5	20	—	—
Example 18	I	90	GPPS*6	10	—	—
Example 19	II	90	HIPS*7	10	—	—
Example 20	I	70	ABS	30	GF*8	10
Example 21	I	60	HISMA	40	GF	10

Table 4 (continued)

	Result of Evaluation				
	Izod Impact Strength (kg·cm/cm)		Tensile Strength	Solvent Resistance (Critical Strain)	Flow Value *9
No.	(23°C)	(-30°C)	(kg/cm^2)	(%)	(ml/sec)
Example 12	70	55	520	0.22	$30x10^{-2}$
Example 13	75	65	540	0.21	$20x10^{-2}$
Example 14	80	75	550	0.26	$6x10^{-2}$
Example 15	80	75	520	0.22	$40x10^{-2}$
Example 16	55	50	460	0.21	$60x10^{-2}$
Example 17	80	30	650	0.25	$5x10^{-2}$
Example 18	75	20	630	0.20	$15x10^{-2}$
Example 19	85	35	650	0.25	$3x10^{-2}$
Example 20	18	12	980	0.23	$18x10^{-2}$
Example 21	20	13	930	0.24	$35x10^{-2}$

Table 5

	PC or PC-PDMS copolymer		Thermoplastic Amorphous Resin		Other Additives	
	kind	Amount (wt%)	kind	Amount (wt%)	kind	Amount (part by weight)
Comparative Example 11	III*10	50	ABS	50	-	-
Comparative Example 12	III	70	ABS	30	-	-
Comparative Example 13	III	60	HISMA	40	-	-
Comparative Example 14	III	80	GPSMA	20	-	-
Comparative Example 15	III	90	GPPS	10	-	-
Comparative Example 16	III	90	HIPS	10	-	-
Comparative Example 17	III	70	ABS	30	GF	10
Comparative Example 18	IV*11	70	ABS	30	-	-
Comparative Example 19	IV	60	HISMA	40	-	-

*10 Toughlon A2200 (molecular weight : 22,000)
Polycarbonate (PC) produced by Idemitsu Petrochemical Co., Ltd.

*11 PC-PDMS copolymer of Preparation Example 5
(n-hexane soluble content : 1.4% by weight)

Table 5 (continued)

	Result of Evaluation				
	Izod Impact Strength (kg·cm/cm)		Tensile Strength	Solvent Resistance (critical Strain)	Flow Value*12
	(23°C)	(-30°C)	(kg/cm^2)	(%)	(ml/sec)
Comparative Example 11	70	40	500	0.22	$6x10^{-2}$
Comparative Example 12	75	50	520	0.21	$4x10^{-2}$
Comparative Example 13	80	60	500	0.22	$7x10^{-2}$
Comparative Example 14	75	15	610	0.20	$5x10^{-2}$
Comparative Example 15	75	10	620	0.20	$3x10^{-2}$
Comparative Example 16	80	20	610	0.20	$3x10^{-2}$
Comparative Example 17	12	8	950	0.23	$3.5x10^{-2}$
Comparative Example 18	70	58	530	0.21	$20x10^{-2}$
Comparative Example 19	75	68	510	0.22	$40x10^{-2}$

*12 Flow Value at 260°C, Load : 100 kg

Examples 22 to 26 and Comparative Examples 20 to 26

[0082] Prescribed amount of PC-PDMS copolymer and fluorine resin shown in Tables 6 and 7 were premixed by a drum tumbler, then supplied to an extruder and kneaded at 290 °C to obtain a polycarbonate resin composition, which was pelletized.
[0083] The pellet obtained was injection molded at a cylinder temperature of 290°C and at a mold temperature of 80°C to obtain a test piece.
[0084] The test piece was determined for Izod impact strength and coefficient of kinematic friction. The results are shown in Tables 6 and 7.
[0085] Notes in Tables 6 and 7 are as follows.

*1 PC-PDMS in Preparation Example 3
*2 PC-PDMS in Preparation Example 4
*3 Polytetrafluoroethylene (Lubron L5), produced by Daikin Industry Co., Ltd.
*4 03MA409C (length : 3 mm, diameter : 13 μm) produced by Asahi Fiber Glass Co., Ltd.
*a Percentage based on the total amount of PC-PDMS and fluorine resin
*b Proportion to the total amount of PC-PDMS copolymer and fluorine resin as 100 parts by weight
*5 Polycarbonate (Toughlon A2200) (molecular weight : 22,000), produced by Idemitsu Petrochemical Co.
*6 PC-PDMS copolymer of Preparation Example 5 having (n-hexane soluble content : 1.4% by weight)
*7 Not determinable under the same conditions because of melting of friction heat
*8 Poor appearance in Comparative Example 23

Table 6

	PC-PDMS copolymer		Fluorine Resin		Other Additives	
	Kind	Amount *a (wt%)	Kind	Amount *a (wt%)	Kind	Amount *b (part by weight)
Example 22	I *1	70	PTFE *3	30	-	-
Example 23	II *2	80	PTFE	20	-	-
Example 24	I	90	PTFE	10	-	-
Example 25	I	80	PTFE	20	GF *4	10
Example 26	II	70	PTFE	30	GF	30

Table 6 (continued)

	Result of Evaluation		
	Izod Impact Strength (kg·cm/cm)		Coeffient of Kinematic Friction
	(23°C)	(-30°C)	
Example 22	16	9	0.10
Example 23	20	10	0.16
Example 24	20	11	0.20
Example 25	13	5	0.19
Example 26	17	7	0.35

Table 7

	PC-PDMS copolymer		Fluorine Resin		Other Additives	
	Kind	Amount (wt%)	Kind	Amount (wt%)	Kind	Amount (part by weight)
Comparative Example 20	III*5	100	PTFE	0	-	-
Comparative Example 21	III	80	PTFE	20	-	-
Comparative Example 22	I	99.5	PTFE	0.5	-	-
Comparative Example 23	II	55	PTFE	45	-	-
Comparative Example 24	III	70	PTFE	30	GF	30
Comparative Example 25	IV*6	70	PTFE	30	-	-
Comparative Example 26	IV	90	PTFE	10	-	-

Table 7 (continued)

	Result of Evaluation		
	Izod Impact Strength (kg·cm/cm)		Coeffient of Kinematic Friction
	(23°C)	(-30°C)	
Comparative Example 20	90	15	-*7
Comparative Example 21	18	5	0.25
Comparative Example 22	70	10	0.40
Comparative Example 23	10	3	0.12*8
Comparative Example 24	12	4	0.45
Comparative Example 25	15	5	0.20
Comparative Example 26	20	6	0.28

Examples 27 and 37 and Comparative Examples 27 and 33

[0086] Prescribed amount of PC-PDMS copolymer and rubber-like elastomer shown in Tables 8 and 9 were premixed by a drum tumbler, then supplied to an extruder and kneaded at 280°C to obtain a polycarbonate resin composition, which was pelletized.

[0087] The pellet obtained was injection molded at a cylinder temperature of 280°C and at a mold temperature of 80°C to obtain a test piece.

[0088] The test piece was determined for Izod impact strength and tensile strength. The results are shown in Tables 8 and 9.

[0089] Notes in Tables 8 and 9 are as follows.

*1 PC-PDMS in Preparation Example 3
*2 PC-PDMS in Preparation Example 4
*3 Paraloid KM330 (acrylic rubber), produced by Rohm & Haas Co., Ltd.

*4 HI-BLEN B611 (acrylic rubber) produced by Nippon Zeon Co., Ltd.
*5 Butyl 268 (butylic rubber) produced by Japan Synthetic Rubber Co., Ltd.
*6 03MA409C (length : 3 mm, diameter : 13 μm) produced by Asahi Fiber Glass Co., Ltd.
*a Percentage based on the total amount of PC-PDMS copolymer and rubber-like elastomer
*b Proportions to PC-PDMS copolymer and rubber-like elastomer as 100 parts by weight

[0090] Notes in Table 9 are as follows.

*7 Toughlon A2200 (molecular weight : 22.000), polycarbonate (PC) produced by Idemitsu Petrochemical Co., Ltd.
*8 PC-PDM copolymer in Preparation Example 5 (n-hexane soluble content : 1.4% by weight)
*a, b The same as above.

Table 8

	PC-PDMS copolymer		Rubber-like elastomer		Other Additives	
	Kind	Amount*a (wt%)	Kind	Amount*a (wt%)	Kind	Amount *b (part by weight)
Example 27	I*1	90	KM330*3	10	-	-
Example 28	I	80	KM330	20	-	-
Example 29	I	90	B611*4	10	-	-
Example 30	I	80	B611	20	-	-
Example 31	I	95	butyl 268*5	5	-	-
Example 32	II*2	90	KM330	10	-	-
Example 33	II	80	KM330	20	-	-
Example 34	II	90	B611	10	-	-
Example 35	II	80	B611	20	-	-
Example 36	II	95	butyl 268	5	-	-
Example 37	II	90	B611	10	GF*6	10

Table 8 (continued)

	Result of Evaluation		
	Izod Impact Strength (kg•cm/cm)		Tensile Strength (kg/cm^2)
	(23°C)	(-30°C)	
Example 27	85	65	630
Example 28	75	65	510
Example 29	85	70	640
Example 30	70	60	520
Example 31	60	55	680
Example 32	90	70	660
Example 33	80	70	540
Example 34	90	75	680
Example 35	75	65	560
Example 36	65	60	720
Example 37	19	10	1030

Table 9

	PC-PDMS copolymer		Rubber-like elastomer		Other Additives	
	Kind	Amount *a (wt%)	Kind	Amount *a (wt%)	Kind	Amount *b (part by weight)
Comparative Example 27	III *7	90	KM330	10	-	-
Comparative Example 28	III	80	KM330	20	-	-
Comparative Example 29	III	80	B611	20	-	-
Comparative Example 30	III	95	butyl 268	5	-	-
Comparative Example 31	III	90	B611	10	GF	10
Comparative Example 32	IV *8	80	KM330	20	-	-
Comparative Example 33	IV	80	B611	20	-	-

Table 9 (continued)

	Result of Evaluation		
	Izod Impact Strength (kg·cm/cm)		Tensile Strength (kg/cm^2)
	(23°C)	(-30°C)	
Comparative Example 27	90	45	630
Comparative Example 28	80	50	510
Comparative Example 29	75	50	520
Comparative Example 30	65	45	680
Comparative Example 31	13	7	1010
Comparative Example 32	75	55	500
Comparative Example 33	60	53	520

[0091] The above tests were carried out under the conditions as follows.

[0092] Izod impact test was carried out in accordance with JIS K-7110, using pellets with a thickness of 1/8 inch at 23 °C and -30 °C.

[0093] Tensile fracture strength test was carried out in accordance with JIS K-7113.

[0094] Solvent resistance test was carried out using a solvent with critical strain according to the 1/4 oval method, and a ratio of volume of toluene/isooctane of 40/60 (in accordance with the method described in Nakatsuji et al., "Shikizai" vol.39, page 455, 1966)

[0095] Flow value was determined in accordance with JIS K-7210 (at 280°C, load : 160 kg or at 260 °C, load : 100 kg).

[0096] Coefficient of kinematic friction was measured under the conditions; phase pressure of 10 kg/cm2, rate of 20 cm/sec., against soft steel (SS-41).

Industrial Availability

[0097] As described above, the polycarbonate resin composition of the present invention can be obtained by blending PC-PDMS copolymer and at least one selected from the group of thermoplastic resin and rubber-like elastomer. According to the polycarbonate resin composition, moldings excellent in low temperature impact resistance, fluidity, sol-

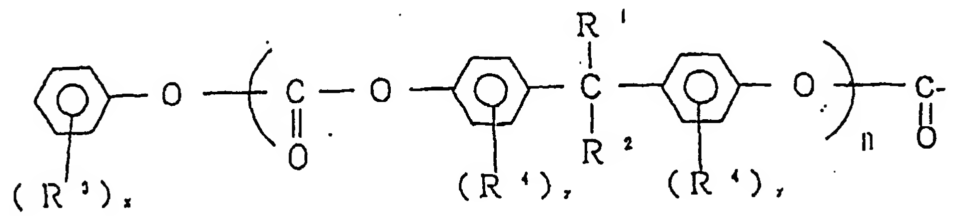
vent resistance, wear resistance and sliding characteristics can be produced.

[0098] Consequently, the polycarbonate resin composition of the present invention is expected to be advantageously used as the materials for moldings which are superior in various physical properties as well as impact resistance.

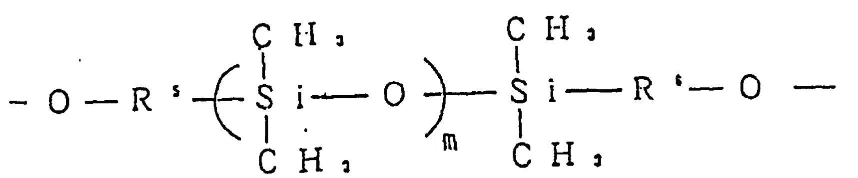
Claims

1. A polycarbonate resin composition which comprises

   (A) 1 to 99 % by weight, 1 to 99 % by weight, 60 to 99 % by weight and 40 to 99 % by weight, respectively, of a polycarbonate/polydimethylsiloxane copolymer comprising a polycarbonate block represented by the general formula (a):

   
   (a)

   wherein R^1 and R^2 indicate independently a hydrogen, an alkyl group having 1 to 4 carbon atoms, R^3 and R^4 indicate independently a hydrogen, a halogen, or an alkyl group or an aryl group having 1 to 20 carbon atoms, x indicates an integer of 1 to 5, y indicates an integer of 1 to 4, and n indicates an integer of 1 to 100, and a polydimethylsiloxane block represented by the general formula (b):

   
   (b)

   wherein R^5 and R^6 indicate independently an organic residue containing aromatic nucleus, and m indicates an integer of 100 or larger,
   said copolymer having 0.5 to 10 % by weight of polydimethylsiloxane block portion and 1.0 % by weight or less of n-hexane soluble content, and a viscosity average molecular weight of 10,000 to 50,000 and
   (B) at least one member selected from the group consisting of

   99 to 1 % by weight of a thermoplastic crystalline resin,
   99 to 1 % by weight of a thermoplastic amorphous resin,
   40 to 1 % by weight of a fluorene resin and
   60 to 1 % by weight of a rubber-like elastomer.

2. A polycarbonate resin according to Claim 1, which comprises (A) 1 to 99% by weight of polycarbonate/polydimethylsiloxane copolymer and (B) 99 to 1% by weight of thermoplastic crystalline resin.

3. A polycarbonate resin composition according to Claim 1, wherein (B) thermoplastic crystalline resin is polyester resin, polyamide resin or polyolefin resin.

4. A polycarbonate resin composition according to Claim 1, which comprises (A) 1 to 99% by weight of polycarbonate /polydimethylsiloxane and (B) 99 to 1% by weight of thermoplastic amorphous resin.

5. A polycarbonate resin composition according to Claim 4 wherein (B) thermoplastic amorphous resin is styrene-based resin.

6. A polycarbonate resin composition according to Claim 1, which comprises (A) 60 to 99% by weight of polycarbonat e/polydimethylsiloxane copolymer and 40 to 1% by weight of (B) fluorine resin.

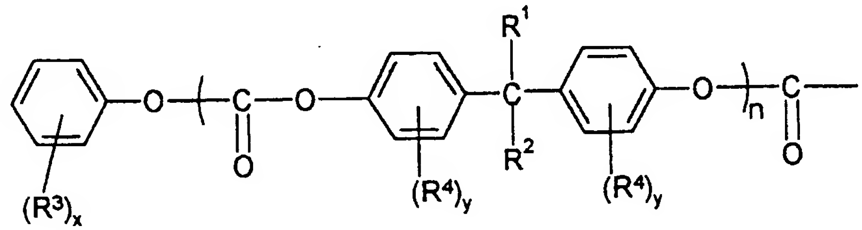
7. A polycarbonate resin composition according to Claim 6,wherein (B) fluorine resin is polytetrafluoroethylene, polychlorofluoroethylene, polychlorotrifluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, hexafluoropropylene-tetrafluoroethylene copolymer or chlorotrifluoroethylene-vinylidene fluoride copolymer.

8. A polycarbonate resin composition according to Claim 1, which comprises (A) 40 to 99% by weight of polycarbonate-polydimethylsiloxane copolymer and (B) 60 to 1% by weight of rubber-like elastomer.

Patentansprüche

1. Polycarbonat-Harzzusammensetzung, die umfaßt:

   (A) 1 bis 99 Gew.-%, 1 bis 99 Gew.-%, 60 bis 99 Gew.-% bzw. 40 bis 99 Gew.-% eines Polycarbonat/Polydimethylsiloxan-Copolymers, das einen Polycarbonatblock, dargestellt durch die allgemeine Formel (a)



(a)

   worin R^1 und R^2 unabhängig voneinander ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen bezeichnen, R^3 und R^4 unabhängig voneinander ein Wasserstoffatom, ein Halogenatom oder eine Alkylgruppe oder eine Arylgruppe mit 1 bis 20 Kohlenstoffatomen bezeichnen, x eine ganze Zahl von 1 bis 5 bezeichnet, y eine ganze Zahl von 1 bis 4 bezeichnet und n eine ganze Zahl von 1 bis 100 bezeichnet, und einen Polydimethylsiloxanblock, dargestellt durch die allgemeine Formel (b) umfaßt:

$$-O-R^5\left(-\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_m\overset{CH_3}{\underset{CH_3}{Si}}-R^6-O- \qquad (b)$$

   worin R^5 und R^6 unabhängig voneinander einen organischen Rest bezeichnen, der einen aromatischen Kern enthält, und m eine ganze Zahl von 100 oder mehr bezeichnet,
   wobei das erwähnte Copolymer 0,5 bis 10 Gew.-% des Polydimethylsiloxanblock-Anteils, einen n-Hexan-unlöslichen Gehalt von 1 Gew.-% oder weniger und ein viskositätsmittleres Molekulargewicht von 10000 bis 50000 aufweist, und

   (B) mindestens einen Bestandteil, der aus der Gruppe ausgewählt wird, die besteht aus:

   99 bis 1 Gew.-% eines thermoplastischen kristallinen Harzes,
   99 bis 1 Gew.-% eines thermoplastischen amorphen Harzes,
   40 bis 1 Gew.-% eines Fluorharzes und
   60 bis 1 Gew.-% eines kautschukartigen Elastomers.

2. Polycarbonatharz-Zusammensetzung nach Anspruch 1, das (A) 1 bis 99 Gew.-% eines Polycarbonat/Polydimethylsiloxan-Copolymers und (B) 99 bis 1 Gew.-% des thermoplastischen kristallinen Harzes umfaßt.

3. Polycarbonatharz-Zusammensetzung nach Anspruch 1, worin das thermoplastische kristalline Harz (B) ein Polyesterharz, ein Polyamidharz oder ein Polyolefinharz ist.

4. Polycarbonatharz-Zusammensetzung nach Anspruch 1, die (A) 1 bis 99 Gew.-% eines Polycarbonat/Polydimethylsiloxan-Copolymers und (B) 99 bis 1 Gew.-% eines thermoplastischen amorphen Harzes umfaßt.

5. Polycarbonatharz-Zusammensetzung nach Anspruch 4, worin das thermoplastische amorphe Harz (B) ein Harz auf Styrolbasis ist.

6. Polycarbonatharz-Zusammensetzung nach Anspruch 1, die (A) 60 bis 99 Gew.-% des Polycarbonat/Polydimethylsiloxan-Copolymers und 40 bis 1 Gew.-% (B) des Fluorharzes umfaßt.

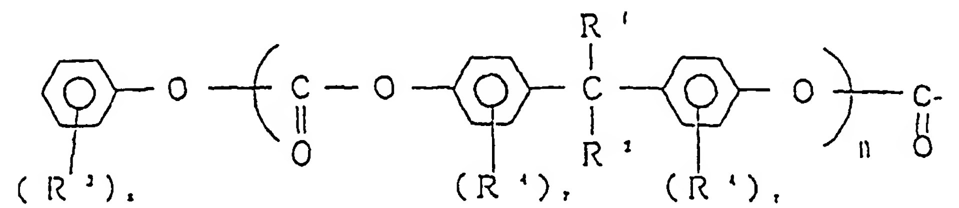
7. Polycarbonatharz-Zusammensetzung nach Anspruch 6, worin das Fluorharz (B) Polytetrafluorethylen, Polychlorfluorethylen, Polychlortrifluorethylen, Polyvinylfluorid, Polyvinylidenfluorid, ein Hexafluoropropylentetrafluorethylen-Copolymer oder ein Chlortrifluorethylen-Vinylidenfluorid-Copolymer ist.

8. Polycarbonatharz-Zusammensetzung nach Anspruch 1, die (A) 40 bis 99 Gew.-% des Polycarbonat-Polydimethylsiloxan-Copolymers und (B) 60 bis 1 Gew.-% des kautschukartigen Elastomers umfaßt.

Revendications

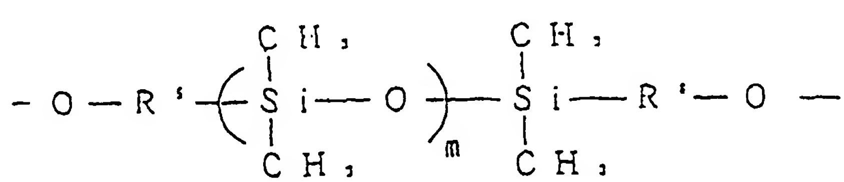
1. Compositon de résine polycarbonate qui comprend

(A) 1 à 99 % en poids, 1 à 99 % en poids, 60 à 99 % en poids et 40 à 99 % en poids, respectivement, d'un copolymère polycarbonate / polydiméthylsiloxane comprenant une séquence polycarbonate.représentée par la formule générale (a):



(a)

dans laquelle R^1 et R^2 représentent indépendamment un atome d'hydrogène, un groupe alkyle comportant 1 à 4 atomes de carbone , R^3 et R^4 représentent indépendamment un atome d'hydrogène, un atome d'halogène ou un groupe alkyle ou un groupe aryle comportant 1 à 20 atomes de carbone, x désigne un nombre entier valant de 1 à 5, y désigne un nombre entier valant de 1 à 4 et n désigne un nombre entier valant de 1 à 100, et une séquence polydiméthylsiloxane représentée par la formule générale (b):



(b)

dans laquelle R^5 et R^6 représentent indépendamment un résidu organique contenant un noyau aromatique et m désigne un nombre entier valant 100 ou plus,
ledit copolymère ayant 0,5 à 10 % en poids de portion de séquence polydiméthylsiloxane et 1,0 % en poids

ou moins de teneur soluble dans l'hexane et une masse moléculaire moyenne en viscosité de 10 000 à 50 000 et
(B) au moins un élément choisi dans le groupe comprenant

99 à 1 % en poids d'une résine cristalline thermoplastique,
99 à 1 % en poids d'une résine amorphe thermoplastique,
40 à 1 % en poids d'une résine fluorée et
60 à 1 % en poids d'un élastomère de type caoutchouc.

2. Résine polycarbonate selon la revendication 1, qui comprend (A) 1 à 99 % en poids de copolymère polycarbonate / polydiméthylsiloxane et (B) 99 à 1 % en poids d'une résine cristalline thermoplastique.

3. Composition de résine polycarbonate selon la revendication 1, dans laquelle (B) la résine cristalline thermoplastique est une résine polyester, une résine polyamide ou une résine polyoléfinique.

4. Composition de résine polycarbonate selon la revendication 1, qui comprend (A) 1 à 99 % en poids de polycarbonate / polydiméthylsiloxane et (B) 99 à 1 % en poids de résine amorphe thermoplastique.

5. Composition de résine polycarbonate selon la revendication 4 , dans laquelle (B) la résine amorphe thermoplastique est une résine à base de styrène.

6. Composition de résine polycarbonate selon la revendication 1, qui comprend (A) 60 à 99 % en poids du copolymère polycarbonate / polydiméthylsiloxane et 40 à 1 % en poids de résine fluorée (B).

7. Composition de résine polycarbonate selon la revendication 6, dans laquelle (B) la résine fluorée est du polytétrafluoroéthylène, du polychlorofluoroéthylène, du polychlorotrifluoroéthylène, du poly(fluorure de vinyle), du poly (fluorure de vinylidène), un copolymère hexafluoropropylène - tétrafluoroéthylène ou un copolymère chlorotrifluoroéthylène - fluorure de vinylidène.

8. Composition de résine polycarbonate selon la revendication 1, qui comprend (A) 40 à 99 % en poids de copolymère polycarbonate - polydiméthylsiloxane et (B) 60 à 1 % en poids d'élastomère de type caoutchouc.